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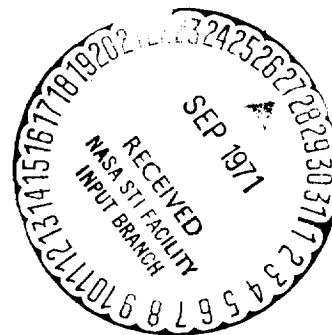
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Cryogenic Properties of a Polyurethane Adhesive*

R. F. ROBBINS†

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado



SUMMARY

Differential thermal analysis (DTA), rebound resilience, and tensile properties of a polyurethane adhesive were measured at cryogenic temperatures. The experimental methods are described, and test results which aid in evaluating the polyurethane for use at low temperatures are discussed. The DTA thermogram reveals that the glass transition temperature (T_g) is 235°K. The resilience profile indicates a resilience minimum (T_r) at 270°K and a frequency of 3800 Hz, which is consistent with the T_g measured by DTA. The low resilience below T_r , caused by secondary low-temperature transitions, shows the high energy absorption capabilities of the polyurethane. Considerable plastic flow at 195°K (40°K below T_g) is evidenced in the results of the tensile tests. The results of the three tests indicate that the polyurethane adhesive will perform well at low temperatures. The test methods should also be useful for evaluating the low-temperature performance of new polymers.

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†Present address: Burger's Express, Inc., 940 Pearl, Boulder, Colorado.

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INTRODUCTION

Due to the rapid increase in potential applications of polymers at low temperature, there is a current need for experimental data which can be used to predict polymer performance in this temperature range. For adhesives these data should define the glass transition temperature (T_g), describe any further transitions below T_g , indicate the strength behavior of the material, and determine the ability of the adhesive to absorb energy. This paper describes test methods developed to generate these data and gives results on a polyurethane adhesive which has shown itself to be quite useful in several low-temperature applications.

The test specimens were prepared from Adiprene-L100* prepolymer by mixing at 344°K with 10 wt% bis(3-chloro-4-amino phenyl) methane [1]. Curing was accomplished by casting the liquid formulation in a flat mold and allowing slow cool to room temperature. The tensile specimens were kept at 344°K for 24 hr. Visual observation showed the samples to be free of bubbles or other defects.

DIFFERENTIAL THERMAL ANALYSIS

In recent years differential thermal analysis (DTA) has been extensively used to study first-order crystallization and decomposition processes in high polymers [2]. This method can also be used to study the second-order glass transition and any additional low-temperature transitions that give rise to a sudden change in heat capacity. The apparatus shown in Fig. 1 was developed to allow highly sensitive DTA measurements from about 6 to 400°K.

The differential thermocouple measures the thermal gradient generated during heating or cooling from a point near the middle of the sample to a point on the surface. A reference material is not needed, since the thermal conductivity of most polymers is low, and a change in heat capacity will therefore occur near the surface before it occurs in the interior. An increase in heating (or cooling) rate will increase the magnitude of the thermal gradient and consequently increase the magnitude of any irregularity due to changes in heat capacity. Other factors which affect the sensitivity of the method, which is basically a diffusivity measurement,

*Trade name, E. I. du Pont de Nemours & Co.

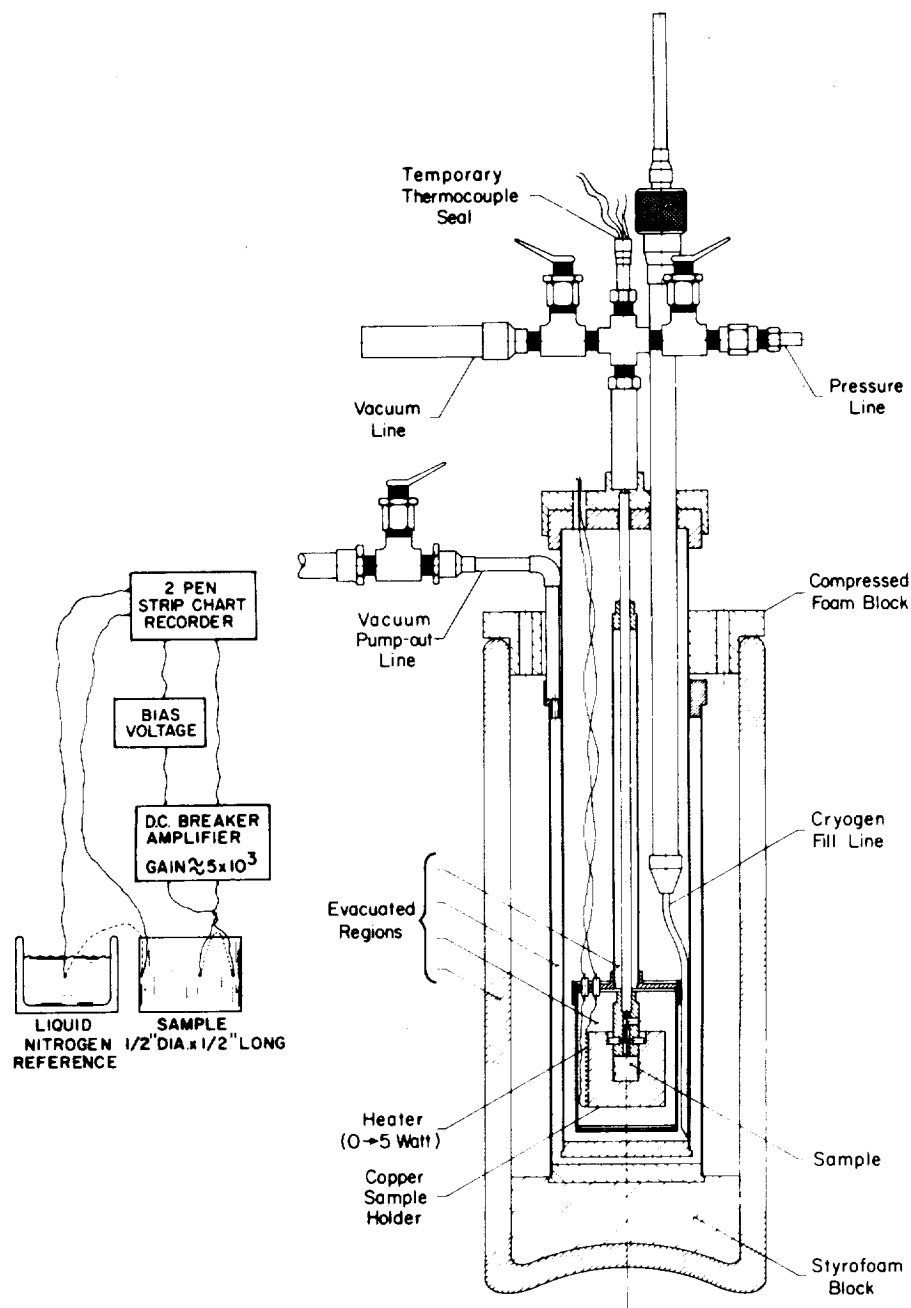


Fig. 1. Differential thermal analysis cryostat.

are sample size, thermocouple sensitivity, and the magnitude of the heat capacity change.

In Fig. 1 the block diagram on the left shows the scheme used to record the thermocouple signals. The voltage ΔE from the differential thermocouple on the sample is amplified from the microvolt range to the millivolt range, and the signal is opposed by an adjustable bias voltage to allow recording on the 10-mV full-scale strip chart recorder without reducing the sensitivity. The random noise generated by the amplifier and bias voltage is less than 50 nV. An additional thermocouple is referenced to liquid nitrogen and connected directly to the recorder, to give a continuous reading of the sample temperature. The thermocouples used were KP (Chromel,* Tophel,† T-1,‡ etc.) versus Au-0.07 at. % Fe. This new thermocouple has a sensitivity of about $15 \mu\text{V}/^\circ\text{K}$ at 10°K , a substantial improvement over other combinations [3].

The cryostat consists of a double dewar with the sample and copper sample-holder enclosed in a vacuum chamber. The heater on the sample-holder allows warming rates from 0.2 to $2.0^\circ\text{K}/\text{min}$. The thermocouple wires pass through the support tube to a room-temperature seal. The support tube also is used to pressurize or evacuate the volume surrounding the sample. During cooling this area is filled with helium gas; during warming, it is evacuated.

Figure 2 shows a typical warming thermogram for the polyurethane adhesive. The sudden drop in ΔE at 235°K is due to the glass transition. Changes above 235°K were merely the return to quasi-equilibrium warming conditions, with the exception of the shoulder at about 273°K which was evidence of absorbed water. The irregularities below 235°K could have been caused by changes in the warming rate; more likely, they were caused by impurities such as residual prepolymer or curing agent. The mechanical properties results will show that this polymer does undergo one or more transitions below T_g , but the step in the thermogram around 210°K is not believed to be caused by one of these. If the interpretations of the β , γ , and δ transitions usually mentioned are correct, the resulting changes in C_p would not be large enough to be evidenced in Fig. 2 [4].

*Trade name, Hoskins Mfg. Co.

†Trade name, Wilbur B. Driver Co.

‡Trade name, Driver-Harris Co.

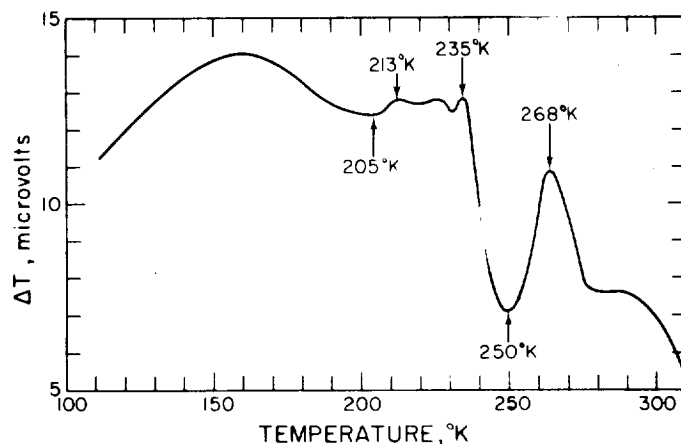


Fig. 2. DTA thermogram, polyurethane adhesive (warming).

REBOUND RESILIENCE

An important property of adhesives is the ability to absorb energy transmitted through the adherends by vibration or other forms of mechanical shock. To study this property, a dynamic mechanical test method is required. Of the many methods in use [5], rebound resilience, was chosen for this test series since the data provide a direct ratio of the energy absorbed to the total energy. The free-fall technique described in the following paragraphs is superior to the more conventional ASTM rebound pendulum [6], since losses in the pendulum arm are eliminated and the apparatus is completely automated.

A steel ball is dropped on a flat polymer sample, and the portion of the impact energy returned to the ball is measured. This can be determined either by recording the rebound height or the ball velocity after impact. The usual method of reporting the data is to find the ratio h_2/h_1 , where h_2 is the rebound height and h_1 is the height from which the ball was initially dropped. The "percent resilience" is then defined as $R = 100 h_2/h_1$. This scheme does not readily lend itself to automation, since the rebound height must be visually observed or photographed for each measurement. Therefore, the alternative of measuring the ball velocity was chosen for the tests described herein. Figure 3 shows the measurement system. The 0.25-in.-diam steel balls drop from a height of 32 in. to impact the sample at the surface of the cryostat, and rebound to a catch basin (not

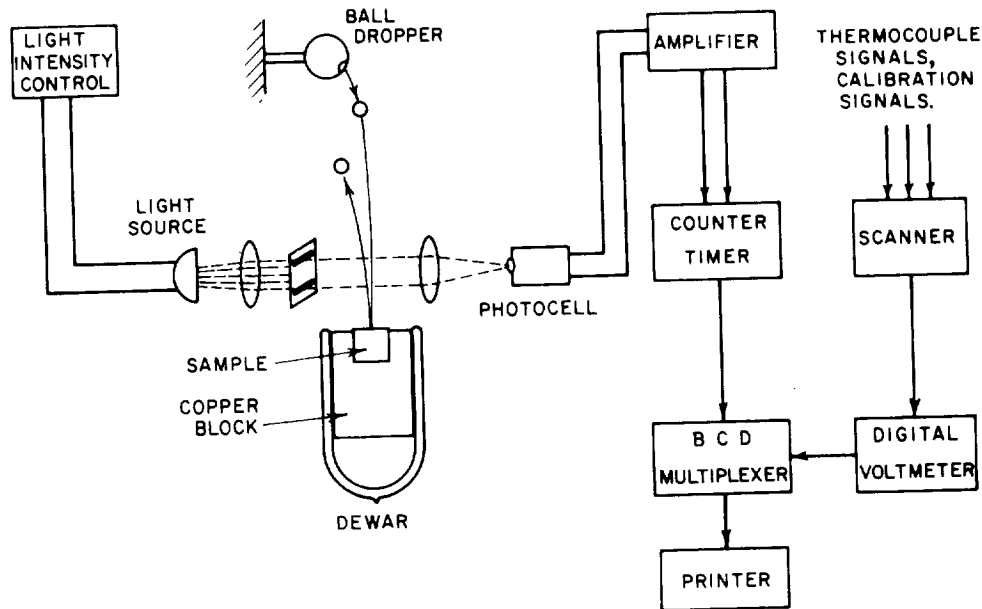


Fig. 3. Rebound resilience data acquisition system.

shown) near the dewar. As a ball rebounds from the sample surface it interrupts the paths of two horizontal light beams passing through slits 0.05 in. wide and 0.3 in. apart, which are focused on the sensing element of a photocell. The resulting signals are used to trigger and then stop a high-speed counter-timer, and the resulting time interval is printed, along with thermocouple signals, using a digital printer. The counter-timer has a resolution of 10^{-6} sec and an accuracy of $\pm 2 \times 10^{-6}$ sec. Since the total time interval between slits is typically 2×10^{-3} sec, the measurement instrumentation introduces a maximum error of about 0.2% in the resilience calculation shown below.

The data can easily be converted to resilience as follows:

$$\% \text{ Resilience} = R = \frac{100 h_2}{h_1} = \frac{100 v_2^2}{v_1^2} \approx \frac{100 t_1^2}{t_2^2}$$

where h is the height of drop or rebound, v is the velocity of the ball before and after impact, and t is the time interval between light beam interruptions by the ball. The subscripts 1 and 2 refer to the drop and the rebound, respectively. A minor correction for the vertical distance from

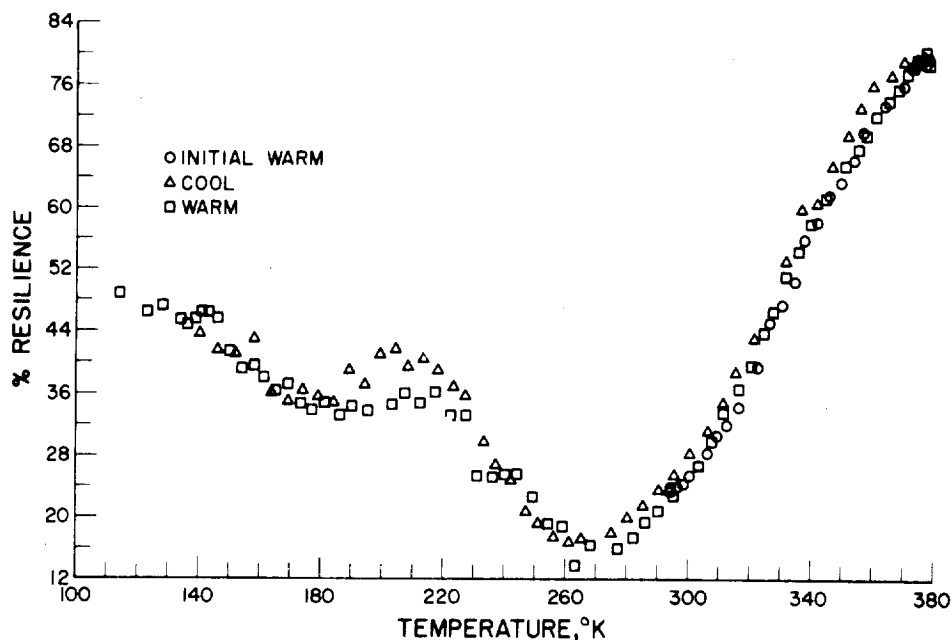


Fig. 4. Thermophysical profile, polyurethane adhesive.

the sample surface to the lower slit (about 1 in.) yields the following more accurate expression:

$$R = 97 t_1^2 / t_2^2 + 3$$

The sample, a solid cylinder 1 in. in diam by 0.5 in. long, is mounted in a copper block which is wrapped with a heater and a cooling coil and inserted in a stainless-steel dewar. The ball dropper is a rotating drum which picks up and subsequently drops one ball every 3 min. At least one thermocouple is inserted in the sample near the impact surface, and the signal is directed to a digital voltmeter and printed after each impact. The maximum error in the temperature measurement introduced by the instrumentation is less than 0.1°K over the entire range.

A typical thermophysical profile generated for the polyurethane adhesive is shown in Fig. 4. All data points are included to indicate reproducibility. Data were taken during an initial heating period followed by cooling to below 100°K and warming. The frequency of the impact, as measured by the audio signal from a microphone mounted near the sample, was about 2500 Hz at temperatures above the resilience minimum at 270°K, and

about 3800 Hz below. The frequency data were taken over the entire temperature range and were constant within 10% both above and below the resilience minimum except for the transition region of $270 \pm 5^\circ\text{K}$. The minimum, which will be designated T_r , is indicative of the glass transition at 3800 Hz. Since an equivalent frequency for the DTA data is not known, the values for T_g and T_r cannot be used to calculate an activation energy for the polyurethane glass transition. However, the values of 235°K (T_g) and 270°K (T_r) agree with an empirical relation based on resilience tests with 10 polymers derived from unpublished NBS data. This relation, calculated from a linear least-squares fit equation, is as follows:

$$T_r = 1.07 T_g + 16.50$$

The slope of this linear relation is nearly identical to that proposed by Lewis and Lewis at low frequencies [7].

The secondary minimum at about 180°K is in part responsible for the unusually low resilience, and therefore the high energy absorption capabilities of the polymer below T_g , and is probably caused by a main chain rotation. The resilience test is a valuable tool for investigating this important property of adhesives. Most amorphous, glassy polymers have resilience values above 70% at temperatures more than 30°K below T_r , and would not perform well in this application.

TENSILE PROPERTIES

In applications where the adhesive must bond effectively in the cryogenic temperature range, the tensile properties are useful. Also, they provide information to complement the dynamic properties data generated by the rebound resilience apparatus. This section describes the tensile tests and presents data at several temperatures in the cryogenic range. Test specimen dimensions are shown in Fig. 5.

Figure 6 shows the tensile cryostat used for the tests. The samples were held by serrated flat plates which were tightened by bolts and a hose clamp. The resulting pressure grip was successful for the tests conducted in the glassy state, but at room temperature the sample extruded at high elongations.

An Instron* testing machine was used with cross-head speeds in the

*Trade name, Instron Mfg. Co.

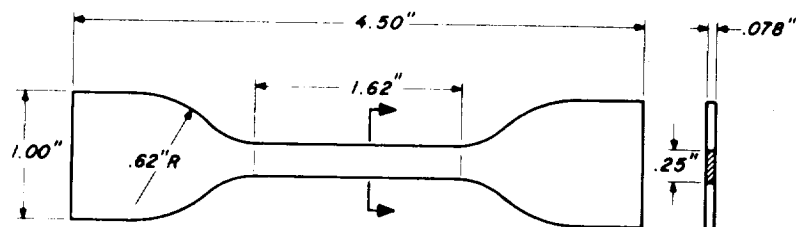


Fig. 5. Polyurethane tensile specimen.

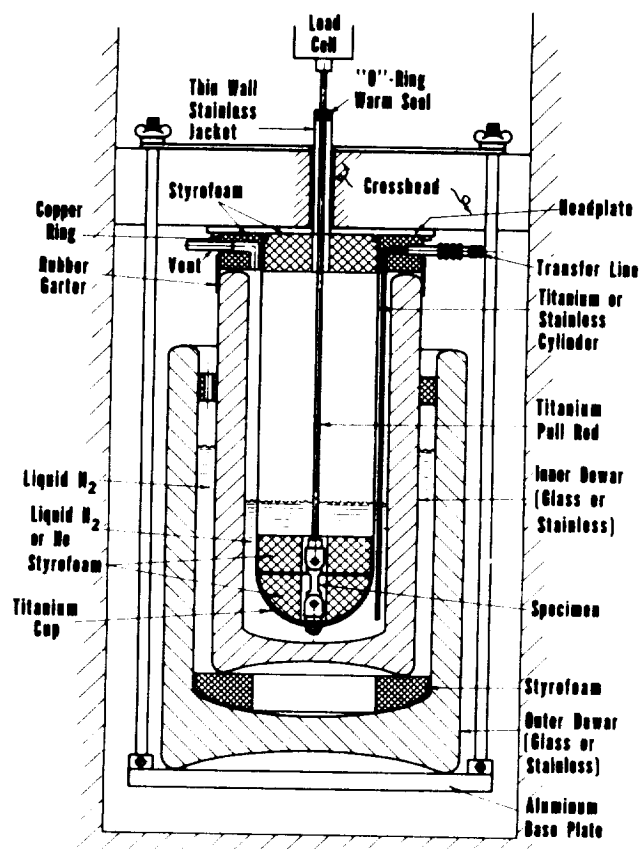


Fig. 6. Tensile cryostat.

range 0.002-20.0 in./min. A 5000-lb load cell was used to record load versus time on a strip chart recorder. Extension was calculated by correlating cross-head speed with chart speed after correcting for cryostat linkage extensions. The linkage correction was less than 10% of the total strain.

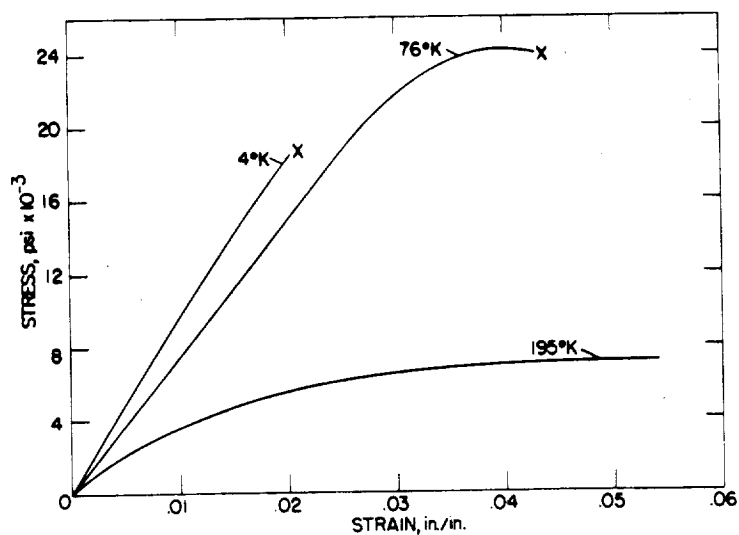


Fig. 7. Stress-strain curves, polyurethane adhesive. Cross-head speed = 0.02 in./min, temperatures as indicated.

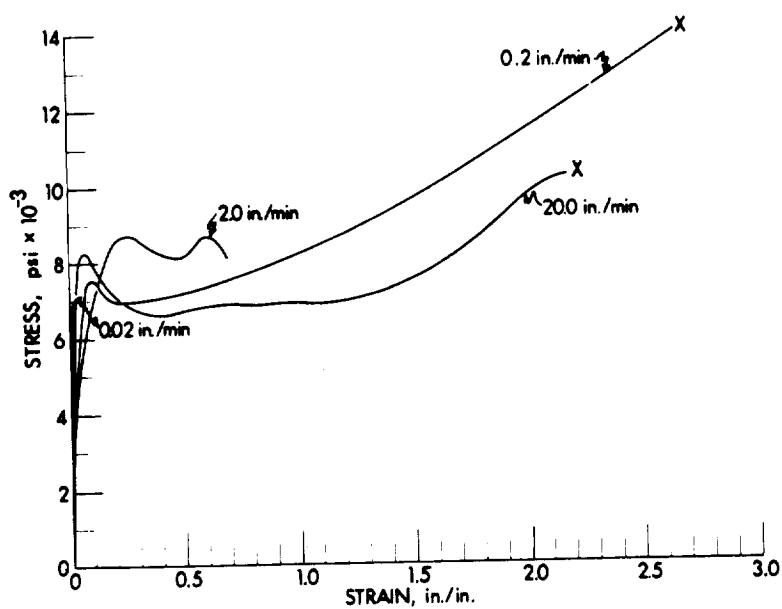


Fig. 8. Stress-strain curves, polyurethane adhesive. Temperature = 195°K, cross-head speeds as indicated.

Three samples were stressed to fracture at 4.0°K, four at 76°K, four at 195°K, and one at 295°K. The 195°K bath was a mixture of ethyl alcohol and solid carbon dioxide in three cases, and nitrogen gas in one case. In the glassy state the alcohol did not affect the polyurethane, as evidence by similar results for the nitrogen and alcohol runs.

The DTA measurements have indicated that the glass transition for the polyurethane adhesive was about 235°K. However, the stress-strain curves indicate elongation at 195°K approaching that expected in the rubbery state. Figure 7 shows typical stress-strain curves at the three test temperatures and a cross-head speed of 0.02 in./min. Since the gauge length for all tests was 1.62 in., this cross-head speed corresponded to a strain rate of about 0.012 min⁻¹. Note the slight plastic deformation at 76°K and the extreme plastic flow at 195°K, 40°K below T_g .

Figure 8 shows results at 195°K and four cross-head speeds. In two cases (at cross-head speeds of 0.2 and 20.0 in./min) the period of plastic yielding was followed by a significant increase in stress at high deformations, due in all probability to a work-hardening or recrystallization phenomenon. The tests at 2.0 and 0.02 in./min were not taken to failure. We do not propose a detailed discussion of these results, but we show the curves to indicate the remarkably high elongation of the specimens. As shown in Fig. 7, this ductility all but disappeared at 76°K; further study between these two temperatures would be valuable but is not easily accomplished with the experimental setup described herein. The dynamic mechanical properties results between 250 and 76°K did show a transition that would occur below 195°K in a low-frequency experiment such as the tensile test. Note in Fig. 7 the drop in ultimate strength at 4°K when compare with 76°K. This phenomenon was also observed in tensile tests on Neoprene discussed by Robbins and Reed [8].

The foregoing tensile tests have served to illustrate the behavior of the polyurethane at several temperatures below T_g . The high plasticity at 195°K shown by the polymer is strong evidence that the material would perform admirably as an adhesive well below T_g . However, the high brittleness and lower ultimate strength at 4°K indicate that at this temperature the adhesive may be subject to cracking and embrittlement similar to other adhesives.

CONCLUSIONS

The foregoing demonstrates that the polyurethane adhesive has high

deformation and energy absorption capabilities well below T_g . These properties are necessary but not sufficient conditions for use of the polyurethane as an adhesive at low temperatures. The experiments described have produced experimental data applicable to performance evaluation. They can be valuable tools for evaluation of future experimental polymers and can provide data useful in developing new and better materials.

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REFERENCES

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Discussion of Paper by R. F. Robbins

Cryogenic Properties of a Polyurethane Adhesive

- S. M. Toy: Did you examine the fractured surface for brittle/ductile behavior?
- R. F. Robbins: The fracture was generally in a plane perpendicular to the load. In some cases the samples fractured in two places, the second fracture being due to the stress propagation at fracture.
- H. M. Doyle: 1) How did you measure the strain in the uniaxial tensile specimens? 2) What gauge length did you use in the calculation of the strain?
- R. F. Robbins: 1) I measured the cross-head travel, and corrected for strains in the cryostat loading members, which were less than 10% of the total strain at all temperatures and loads. 2) The initial gauge length (1.62 in.) was used to calculate all strains.
- R. F. Landel: Will the ball leave a permanent indentation? The indentation (and hence orientation) thus induced could affect the resilience, and this could explain the difference between the "cooling" and "reheating" curves.
- R. F. Robbins: The ball, after a number of bounces, does produce irregularities in the surface. This does not grossly affect resilience values, but it could be responsible for the "weakening" of the 180°K transition on warming.
- J. Philipson: In the test where you use a bouncing ball to determine the resilience of the elastomer, does not the impact of the ball cause a local heating in the sample which will cause an instantaneous warming and affect the resiliency of the material?
- R. F. Robbins: The warming does indeed occur; but since balls are bounced with a 3-min interval, the heat is completely

transferred to the copper block and does not affect subsequent tests.

J. Hertz: What sort of scatter did you observe in your 4°K tensile tests versus the results obtained at 77°K.

R. F. Robbins: A much higher scatter ($\pm 10\%$) at 4°K. However, no 4°K fracture strength was as high as the lowest 76°K (LN₂ boiling point at Boulder, Colo.) point.